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FOURTH QUARTERLY R&D STATUS REPORT

Principal Investigator:
Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania

REPORTING PERIOD: 6/15/87 - 9/30/87

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Office of Research Administration
Suite 300 Mellon Building
133 S. 36th Street
Philadelphia, PA 19104-3246

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OF CONTRACT: 9/15/86

EXPIRATION DATE
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TELEPHONE NO.: 215-898-8307 or 215-898-6323

SHORT TITLE OF WORK: **Conducting Electronic Polymers by
Non-Redox Processes**

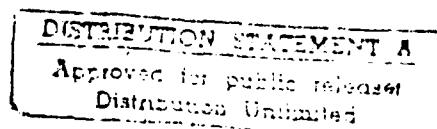
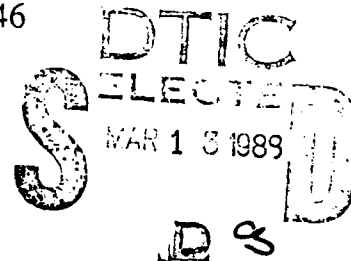


Table of Contents

I.	Research Groups	1
II.	Description of Progress	2
	1. University of Pennsylvania	2
	2. The Ohio State University	5
	3. Lockheed Advanced Aeronautics Corporation	7
	4. Massachusetts Institute of Technology/ Rensselaer Polytechnic Institute	9
	5. University of Rhode Island	9
	6. Montclair State College	10
III.	Working Relationships Involving University of Pennsylvania Personnel and Those of the Subcontractors	11
IV.	Miscellaneous Scientific Interactions of Key Personnel Associated with the Program	12
V.	Publications	15
	1. Published Papers	15
	2. Papers accepted/submitted for publication	16
VI.	Patents	17
VII.	Contractual Administration	17
VIII.	Changes in Personnel	18
	1. University of Pennsylvania	18
	2. The Ohio State University	19
	3. Lockheed Advanced Aeronautics Corporation	19

4. Massachusetts Institute of Technology/ Rensselaer Polytechnic Institute	19
5. University of Rhode Island	19
6. Montclair State College	20
IX. Fiscal Status	21



DATE	10/30
TIME	10:30
BY	J.C.
REMARKS	per call J.C.
INITIALS	A-1

I. Research Groups*

1. University of Pennsylvania
 - (a) Department of Chemistry (A.G. MacDiarmid)
 - (b) Department of Materials Science (G.C. Farrington)
2. The Ohio State University
Department of Physics (A.J. Epstein)
3. Lockheed Advanced Aeronautics Corporation
Aeronautics Systems Group Research (T.S. Kuan)
4. Massachusetts Institute of Technology/
Rensselaer Polytechnic Institute
Department of Chemistry (G.E. Wnek)
5. University of Rhode Island
Department of Chemistry (S.C. Yang)
6. Montclair State College
Department of Chemistry (B.D. Humphrey)

*Financial information for each group given in Section IX.

II. Description of Progress

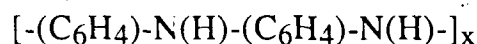
1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

(i) Summary of Progress

^{15}N NMR Spectra of Polyaniline*

In order to gain additional information concerning the nature of doped and undoped polyanilines, a collaborative ^{15}N NMR study is underway with Professor S.J. Opella, Chemistry Department and Dr. Opella's postdoctoral associate, Dr. K.V. Ramanathan, (half of whose salary is paid by MacDiarmid's DARPA contract). ^{15}N -enriched leucoemeraldine base ($y=1$) i.e.



(compound I), "emeraldine" base ($y \approx 0.5$), (compound II); protonated "emeraldine" base, i.e. emeraldine $\cdot\text{qHCl}$ and (compound III) were synthesized.

The solid state ^{15}N NMR CP/MAS in natural ^{15}N abundance of the model compound, $-(\text{C}_6\text{H}_4)-\text{N}(\text{H})-(\text{C}_6\text{H}_4)-\text{NH}_2$, exhibited signals at 70 ppm and 37 ppm (ammonium sulfate reference) characteristic of the $-\text{N}(\text{H})-$ and $-\text{NH}_2$ groups respectively.

The solid state spectrum of compound I exhibited only one peak (at 54 ppm) characteristic of the $-\text{N}(\text{H})-$ groups. It is, therefore consistent with the proposed structure of the polymer.

The solid state spectrum of compound II, showed only an absorption characteristic of the $-\text{N}(\text{H})-$ region at 62 ppm with a shoulder at ~ 35 ppm. The expected $-\text{N}=\text{N}-$ peak was absent. However, the spectrum (by pulsed FT-NMR) in solution in NMP/DMSO- d_6 showed two chief $-\text{N}(\text{H})-$ peaks at 54 ppm and 62 ppm in addition to the expected $-\text{N}=\text{N}-$ peak at 321 ppm. Studies are presently underway to ascertain why the $-\text{N}=\text{N}-$ peak was observed in solution but not in the solid state. It may be noted that the shoulder at ~ 35 ppm in the spectrum of the solid is absent in the spectrum of the solution in which the principal absorptions in the $-\text{N}(\text{H})-$ region are at 54 ppm and at 62 ppm. Analysis of the spectra are not yet complete but the solution spectrum suggests the possible presence of two adjacent reduced groups in the polymer, which would be expected if $y > 0.5$.

(2)

Preliminary studies of compound III show that it exhibits a broad overlapping multiple line structure ranging from ~60 ppm to ~300 ppm, the characteristics of which vary with the extent of protonation. The extent of protonation present in this sample was not clearly defined; however, the results are consistent with those expected for the protonation of a paramagnetic species on protonation.

*Supported in part by (i) NSF Grant No. DMR-85-19059 and by NIH Grant #GM-24266 to Professor S.J. Opella.

Solution-Processibility and Casting of Free-Standing Films of Polyaniline*

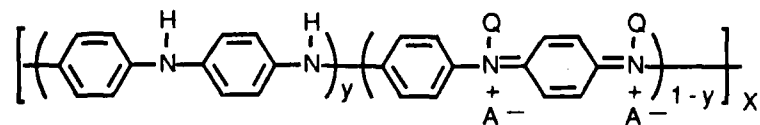
→ For many years a major draw-back of conducting polymers was that they were not processible. However, we have now found that emeraldine base may be dissolved in 80% aqueous acetic acid or N-methylpyrrolidinone (NMP) from which free-standing films of emeraldine acetate and emeraldine base may be cast. In the latter case, after appropriate treatment, free-standing, lustrous, coppery, flexible films of emeraldine base up to 12 cm x 12 cm may be obtained. They are shiny on both sides and are usually 0.01 - 0.04 mm thick. they contain no pinholes or tears. Upon creasing these films firmly between two fingernails, they return to their original shape without breaking. The mechanical properties of the films suggest that at least a portion of the polymer must be present as a relatively high molecular weight component. When shaken the films "rattle" in a manner similar to aluminum foil! These films ($\sigma \sim 10^{-10}$ S/cm) can be protonated i.e. "doped" to the metallic conducting regime ($\sigma \sim 1-5$ S/cm) by aqueous 1M HCl.

In addition to demonstrating the processibility of polyaniline, these studies provide the polymer in a form very much more convenient for many physics studies than the previously used powder form.

*Supported in part by NSF Grant No. DMR-85-19059.

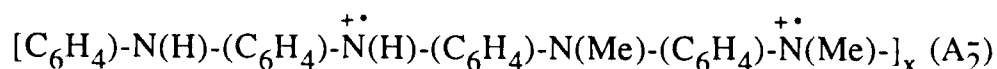
"Pseudo-Protonic Acid" Doping of Polyaniline*

The "doped", (protonated) highly conducting form of polyaniline can be written in the form



where $y = 0.5$, $Q = H$ and A^- = an anion. Doping is accomplished by treating the corresponding base form with a protonic acid such as H^+Cl^- , the H^+ attaching to the $-N=$ nitrogen sites. We have been successful in synthesizing a

series of polyanilines the final constitution of which may be regarded as being obtained by the attachment of an R^+ group ($R = \text{Me}, \text{Ph}$), instead of an H^+ to the $-N=$ sites. Chemical oxidative polymerization of PhN(H)R [where $R = \text{Me}, \text{Ph}$, $p\text{-(NaO}_3\text{S)}^+y(\text{C}_6\text{H}_4)$] result in intense green materials of the type $[-(\text{C}_6\text{H}_4)\text{-N(R)-}]^+y\text{Cl}^-_y$ (I) (where $R = \text{Me}, \text{Ph}$) having conductivities of 10^{-3} and 10^{-2} S/cm respectively when $y = 0.46$ and 0.58 respectively by elemental analysis. Reduction by N_2H_4 of the polymer in which $R = \text{Me}$ results in the formation of the pale yellow material believed to be $[-(\text{C}_6\text{H}_4)\text{-N(R)-}]_x$ (II). The cyclic voltammograms of compounds (I) and (II) in 1.0M HCl consist of one peak whose $E_{1/2}$ is 0.41V vs. SCE. Reaction of emeraldine base, $[-(\text{C}_6\text{H}_4)\text{-N(H)-}(\text{C}_6\text{H}_4)\text{-N(H)-}(\text{C}_6\text{H}_4\text{-N}=\text{(C}_6\text{H}_4)=\text{N-})_x]$, with Me_2SO_4 on the vacuum line results in materials which can be formulated as polysemiquinones viz.,



where $A^- = (\text{MeSO}_4)^-$, ($\sigma \sim 10^{-2}$ S/cm). The extent of methylation can be controlled by the reaction time. The polymer exhibits a Pauli susceptibility (6.25×10^{-5} emu/mole of 2 rings) approximately half that of the corresponding emeraldine $\cdot\text{HCl}$.

*Supported in part by NASA Grant No. NAG10-0025.

(ii) Major Equipment Purchased or Constructed

Contributed \$15,000 (~ 50% of total cost) on 8/19/87 toward purchase of signal averager and pulse programmer for collaborative ^{15}N NMR studies with Professor Stanley Opella, Department of Chemistry, University of Pennsylvania.

b. Department of Materials Science and Engineering (Farrington)

(i) Summary of Progress

Dr. Ching-min Wu has completed his investigations of the optical spectroscopy of dissolved polyaniline and short-chain polyaniline model compounds. In the coming months, Dr. Wu will begin a detailed study of the influence of electrochemical synthesis conditions on the purity, structure, and morphology of polyaniline. In this study, he will use conventional electrochemical techniques as well as electrolysis at a rotating ring-disk electrode.

Mr. Jonathan Foreman has also begun his Ph.D. research, which initially will be an investigation on the reductive electrochemistry ('n-doping') of polyacetylene with novel dopants (monovalent, divalent cations, and complex ammonium ions) as well as with ultra-pure and oriented polyacetylene.

Ms. Hong Yang has begun her Ph.D. research into ion diffusion and structure of network polyethylene oxide [PEO] into which salts of divalent cations and monovalent anions are dissolved. In the past several months, she has successfully synthesized films of network PEO, measured their thermal properties and crystallinity, and incorporated divalent salts in them.

2. The Ohio State University

Department of Physics (Epstein)

(i) Summary of Progress

We have made significant progress in our studies of the physical properties of conducting polymers, concentrating our efforts on the evolution of the electronic structure of the polyaniline system with changes in proton and electron concentration. The techniques used to do this are optical absorption spectroscopy and photoinduced optical absorption spectroscopy. We have now extended our photoinduced optical absorption studies of emeraldine base polymer (previously reported in the third quarter R&D status report) to probe energies further in the infrared and ultraviolet. The new results are very enlightening. As previously reported, the emeraldine base sample is exposed to a pump laser source at ~ 2.5 eV (exciting electrons into the exciton band). We previously reported this result in a bleaching of the exciton band and the introduction of two new photoinduced absorptions at 1.5 eV and 3 eV. These photoinduced absorptions were associated with the positive polaron which is observed in chemically protonated emeraldine base material. Extending the photoinduced absorption studies toward the ultraviolet, we now observe the existence of a bleaching beginning at ~ 3.5 eV. This bleaching extends up toward 5 eV. We currently assign this bleaching to a bleaching of the interband transition similar to the bleaching of the interband transition which occurs in polyacetylene or polythiophene upon photoexcitation of solitons and polarons. Extending the probe energy toward the infrared, we now observe another photoinduced absorption to excitation from negative polaron levels formed during the photodissociation of the exciton to the empty conduction band states. Together these data show that emeraldine base has a very unusual photoinduced response when pumped with light of energy 2.0-2.5 eV, resulting in three photoinduced absorption bands and two photoinduced bleaching bands. We have now begun to extend these results to photoinduced absorption studies

on emeraldine salt polymer and solutions of emeraldine base and emeraldine salt. Considerable effort has been put into measuring the temperature and time profiles of each of these photoinduced bleaching and absorption peaks in an effort to understand the kinetics of the defect states induced in these polymers.

An effort has been placed in analyzing the low temperature electron spin resonance studies performed on polyaniline and on $(\text{CHD}_y)_x$. This work in collaboration with Professor J. Gaines (OSU, now at University of Hawaii) shows that the electron (neutral soliton) spins in $(\text{CH})_x$ diffuse primarily in one dimension. Careful analysis of the temperature dependant line shapes indicates that the addition of 16% CHD units to the chain interrupts the spin diffusion to the extent that the line shape changes substantially and the primary spin diffusion is now three dimensional. It should be noted that the spin diffusion rate is also two orders of magnitude slower than it is when it is one dimensional in the absence of the CHD units. EPR line shape analysis for the emeraldine base polymer indicates that for this system, the spin diffusion is always three-dimensional.

We have been extending and carefully reproducing our experimental studies of the temperature dependant microwave conductivity and dielectric constant of the emeraldine polymer as a function of protonation. In particular, we have been emphasizing the measurement of the dielectric response as a function of protonation of a single sample. This is done so that we can normalize appropriately for the depolarization factors which would otherwise lead to uncertainties in the experimental analysis. Our results now show that the dielectric constant of emeraldine salt can be as high as several hundred. The high dielectric constant, combined with the relatively high conductivity of this material, leads to an enormously large dielectric loss at microwave frequencies. We have also been studying the change in dielectric constant and microwave conductivity as a function of pumping (removal of H_2O). The results show that the microwave conductivity tracks dc conductivity in that both decreased by a factor of approximately three on the same time scale. The dielectric constant also decreases. These results, with the frequency independence of the conductivity up to 1010 Hz, have been used to demonstrate that the proton exchange assisted conductivity mechanism proposed by the Grenoble group is not appropriate for the emeraldine polymer series. Instead we propose that the primary effect of the water is to affect the permeability of the barriers that exist between the conducting polymer islands that occur upon protonation of the polymer. Initial studies of the temperature dependence of the conductivity with and without pumping indicate that the dc conductivity continues to be dominated by charging energy limited tunneling with the effectiveness of the tunneling barrier being much less in the presence of water.

(ii) Major Equipment Purchased or Constructed

The FTIR and EPR spectrometers have arrived and have been installed. The picosecond apparatus is being assembled, as well as the steady-state laser equipment. Renovation of the optics laboratory has been completed. Orders have been placed for a potentiostat/galvanostat, a programmable current source, and a continuous flow liquid helium refrigerator.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

(i) Summary of Progress

During this last quarter our group has been performing research in two separate directions. These two research areas encompass the synthesis and basic structural studies of polyaniline oligomers and the thermal degradation of polyaniline. These topics were selected since they both have significant importance for basic studies of polyaniline as well as being important for applications in the aerospace industry.

The oligomer research is primarily being performed by Mr. Ben Mattes as part of his Ph.D. thesis. Ben is working at Lockheed while performing his graduate work at UCLA under the guidance of Dr. Rick Kaner. Ben will be performing basic structural studies of polyaniline oligomers rather than high molecular weight polyaniline since the purity of the smaller molecules can be better controlled.

Lockheed's interest in polyaniline oligomers include the use of the free-base as a non-linear optical material and the use of the oligomers in oligomers which can be incorporated into the backbone of common structural materials (polyimides, bismaleimides, polyamides etc.) This work should lead to the development of conductive polymers with excellent mechanical properties.

As a starting point for the oligomer synthesis, we have synthesized tetraniline. We chose a variation of Honzl's method, which involves the coupling of aniline dimers with a succinic ester. Via this procedure we attained the product which was characterized by FTIR, UV-VIS and NMR. The octomer and hexamer should be synthesized by the end of next quarter.

We are also currently working the synthesis of amine terminated polyaniline oligomer. Initial studies seem hopeful, however more time is needed for this synthesis to be worked out.

Our research on the thermal degradation of polyaniline was motivated by strict thermal stability requirements for many potential applications of conductive polymers. Our first goal was to see if polyaniline could possibly be used for extended periods of time in the range of 150-200° C. As part of the URI project we studied the thermal stability of polyaniline.

We found polyaniline emeraldine free-base to undergo significant oxidation after 24 hours at 180° C in air. This product could not be rendered conductive by doping with aqueous tosylic acid and was not soluble in aqueous formic or acetic acid solutions as is the emeraldine free-base. FTIR and UV-Vis studies suggested that the product is an overoxidized polyaniline structure. Heating in argon was not found to lead to the same significant decomposition.

We found that when doped with an acid, the primary decomposition pathway is loss of the acid due to decomposition or evaporation of the acid. However, we found if a thermally stable, nonvolatile acid is used, the conductive polyaniline is very thermally stable. For example if the polyaniline is derivatized with *m*-benzene disulfonic acid, the conductivity drops insignificantly after 24 hours at 180° C in air and very little change is seen in the UV-Vis and FTIR spectra. In comparison, the conductivity of polyaniline derivatized with tosylic acid drops by over 3 orders of magnitude and significant changes are seen in the absorption spectra after 24 hours under the same conditions. One interesting fact is that when the oxidative stability of the emeraldine free base is compared to that derivatized with *m*-benzenedisulfonic acid, one sees that the polyaniline backbone is more stable in air when doped with an acid than as the free-base. The acids actually protect the polyaniline backbone from oxidation. This work is complimented by the fact that the oxidation potential of polyaniline emeraldine is found to increase when the pH of the solution is decreased. These studies prove that polyaniline is a candidate for high service temperature applications. Further studies in this area will include studying the thermal stability of completely alkylated polyaniline and designing forms of conductive polyaniline which have both high thermal stability and processibility.

Although we noted in the last quarterly report that we had begun studies on aligning polyaniline/nylon blends, we found our crude techniques were not efficient at completely aligning the polyaniline. We are currently working on attaining an outside contractor to perform the poltrusion of polyaniline films. We will perform this with pure polyaniline films from NMP and with blends we have

developed as part of Lockheed's Internal Research and Development (IRAD) program on conductive polymers.

4. Massachusetts Institute of Technology/Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

(i) Summary of Progress

The Program at MIT was completed over the summer with the move of Prof. Wnek to RPI and the thesis submissions of Duncan H. Whitney (now at Polaroid Corp., Cambridge, MA) and Walter W. Focke (now at NMIR, Pretoria, South Africa). Our post-doctoral research assistant, Dr. Yen Wei, has taken a position as Assistant Professor of Chemistry at Drexel University. A paper on Whitney's work entitled "Reactions of N-Type (Reduced) Polyacetylene With Alkyl Halides" has been accepted for publication in *Macromolecules*, and a patent has been issued (assigned to MIT) on our method of functionalizing polyacetylene with alkyl groups (G. E. Wnek and D. H. Whitney, "Substituted Acetylenic Polymers and Conductive Materials Formed Therefrom," US 4,672,093, June 9, 1987). Also, a paper with Focke and post-doctoral research assistant Yen Wei, entitled "The influence of Oxidation State, pH and Counterion on the Conductivity of Polyaniline," has been accepted in the *Journal of Physical Chemistry*. A joint paper (MacDiarmid, Ray, Focke, Wei, Wnek) on the synthesis and electrochemistry of ring alkylated polyanilines is being written. Dr. Focke has suggested that the so-called capacitive currents observed in cyclic voltammograms of polyaniline are more reasonably rationalized in terms of a finite density of states at the Fermi level rather than charging of high surface area fibrils. The details of the argument are given in his thesis.

A graduate student at RPI has elected to work on conductive polymers with the support from our subcontract. Experiments should be underway by about the middle of October.

5. University of Rhode Island

Department of Chemistry (Yang)

(i) Summary of Progress

Three graduate students have been supported as half time research assistants during the summer. Their works are briefly described:

Richard Cushman made detailed studies of the pH-potential phase diagram with particular emphasis on the conductive form of polyaniline. He has obtained clear indication of the existence of optically distinguishable sub-forms within the conductive phase. The study indicates that there is a doping induced electronic structural transformation between two spectroscopically recognizable conductive forms. It is of interest to see if they are related to the Curie and Pauli spin sub-forms discovered by Professors Epstein and MacDiarmid.

Robert Clark has completed the optical spectra measurements on several ring substituted polyanilines. He found that the methyl and methoxy substituents have significant effect on the switching potentials for the electrochemical doping process and the protonic doping process.

Brian Schmitz has made measurements on the spectroscopic properties of an N-substituted polyaniline: poly-(N-phenylbenzylamine). Preliminary results indicate that N-substitution may prohibit the formation of one of the quinonediimine forms.

Two other students not directly supported by this subcontract are working on the morphological modification of polyaniline and the kinetics of the doping induced property switching. Jyun H. Hwang used electron microscopy to study the morphology of polyaniline fibers. He found that he can control the morphology consistently by using different conditions for polymer growth. The major controllable factors are the fiber diameters and how the fibers are woven into networks. Diana Zhang studied the time resolved visible and near-IR spectrum. She measured the evolution of absorption spectra during potential-jump conditions. A pH-potential phase diagram for the switching rate constants is constructed. The goal is to understand the long time polymer dynamics of the doping process so that the switching speed can be improved.

6. Montclair State College

Department of Chemistry (Humphrey)

(i) Summary of Progress

Research has centered on a new group of graft copolymers/composites discovered at MSC composed of a polysaccharide matrix and a conducting polymer. Both the polysaccharide matrix and the conducting polymer have been varied, as well as the method of producing the films, resulting in polymeric materials exhibiting a wide range of physical and

chemical properties. These composites have the mechanical properties of the polysaccharide (flexible and tough) and the electronic properties of the conducting polymer (UV-vis characteristics and conductivity). During the final quarter these materials have been used in the cuprammonium and viscose processes for the synthesis of rayon thread. It has been demonstrated that these processes could lead to the synthesis of conducting rayon thread. Both polypyrrole and polyaniline composites have been used resulting in the formation of black and green thread respectively. These materials (and the processes used to synthesize them) are being investigated because they meet many of the overall goals of my project which is to synthesize conducting polymers that will be of biomedical importance and/or utility.

(ii) Major Equipment Purchased or Constructed

During the final quarter the equipment received at Montclair State consisted of a Hewlett Packard printer and necessary chemicals (pyrrole, aniline, ammonium persulfate, sodium chloride, platinum, ceric ammonium sulfate, polysaccharides, etc.) to continue research.

III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

1. Dr. C. M. Wu of Dr. G. C. Farrington's group and Dr. K. V. Ramanathan of Dr. S. J. Opella's group attended some of Dr. MacDiarmid's group meetings and guest's lectures.
2. Aug. 20, 1987, Dr. B. D. Humphrey of Montclair State College visited the laboratory of Dr. A. G. MacDiarmid.
3. Aug. 31, 1987 Dr. Randy Cameron of Lockheed Corporation met with Dr. Brian Humphrey of Montclair State College in Princeton, NJ.
4. Sept. 1, 1987, Dr. Randy Cameron of Lockheed Corporation, California visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Dept. of Chemistry.

5. Sept. 8 & 9, 1987, Dr. A. G. MacDiarmid and his group from the University of Pennsylvania, Chemistry Department and Dr. A. J. Epstein and his group from OSU held a joint group meeting at Somerset, PA.

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. June 16, 1987, Dr. Mark Herbst of the Office of the Deputy Undersecretary of Defense (Research and Advanced Technology), The Pentagon, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania. Dr. A. J. Epstein of OSU and Dr. B. D. Humphrey of Montclair State College attended this meeting.

2. June 24-26, 1987 Dr. A. J. Epstein gave an invited lecture to the Ohio Regional American Chemical Society Meeting in Columbus, Ohio, entitled "Conducting Polymers: Chemistry and Physics."

3. June 26, 1987, Dr. A. G. MacDiarmid gave an invited talk to the Chamber of Commerce of the City of Philadelphia on "Conducting Polymers and Academic Research."

4. June 30 to July 3, 1987, Dr. A. G. MacDiarmid gave an invited lecture entitled "Polyaniline: A New Concept in Conducting Polymers," at the Adriatico Research Conference on One-Dimensional Organic Conductors: Chemistry, Physics and Applications, in Trieste, Italy. Dr. A. J. Epstein presented an invited talk entitled "Ferromagnetism in Polymers."

5. July 6, 1987, Dr. A. J. Epstein visited the laboratory of Dr. H. Naarmann of BASF in West Germany.

6. July 13&14, 1987, Dr. Serge Lefrant of the University of Nantes, Montpellier, France, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry. Title of the talk given: "Resonance Raman Spectra of Conducting Polymers."

7. July 19, 1987, Dr. Hideki Shirakawa of the University of Tsukuba, Japan, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry.

8. July 19, 1987, Dr. Patrick Bernier of the CNRS, France, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry. Title of the talk given: "Magnetic properties of $(CH)_x$."
9. July 27, 1987, Dr. Kaoru Iwata of Teijin, Ltd., Japan, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry. Title of the talk given: "Electrically Conducting Polymers."
10. July 29, 1987, Dr. William R. Salaneck of Linköping Institute of Technology, Sweden visited the laboratory of Dr. A. G. MacDiarmid at the Department of Chemistry.
11. August 7, 1987, Dr. Nick Castellucci of Northrup Corp., California, visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry.
12. August 11, 1987, Dr. A. G. MacDiarmid and his entire group attended a lecture by Dr. Brian Vincent of the University of Bristol, England entitled "Preparation and Properties of Electrically Conducting Polymer Latices" at the du Pont Marshall Laboratories in Philadelphia.
13. August 12, 1987, Dr. Patrick Bernier of CNRS, France, visited Dr. MacDiarmid's laboratory. Title of the talk given: "NMR of $(CH)_x$ and Derivatives."
14. August 12, 1987, Dr. Brian Vincent of the University of Bristol, England, visited Dr. MacDiarmid's laboratory.
15. August 12, 1987, Dr. Daniel Sandman of GTE Co., Valley Forge, PA, visited Dr. MacDiarmid's laboratory.
16. August 13, 1987, Dr. Evelina Mulazzi of the Università degli studi di Milano, Italy visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry. Title of talk given, "Resonance Raman Scattering Frequencies of the Stretched and Unstretched Polyacetylene Films."
17. August 18, 1987, Dr. Randy Cameron of Lockheed Corporation, Valencia, CA, visited Dr. MacDiarmid's laboratory. Title of the talk given: "Recent Developments in Conducting Polymer Field at Lockheed."

18. August 21-24, 1987, Dr. A. J. Epstein visited Xerox Corp. in New York to consult with Dr. E. Conwell, Dr. C. Duke and Dr. M. Rice.
19. August 24 to 27, 1987, Dr. A. G. MacDiarmid gave an invited lecture at the Molecular Electronics and Biocomputers Satellite Symposium in Budapest, Hungary. Title of talk given: "Synthetic Metals: A New Role for Organic Polymers".
20. August 30 to September 3, 1987, Dr. A. G. MacDiarmid gave an invited lecture at the American Chemical Society Meeting in New Orleans, Louisiana. Title of talk given there: "Synthetic Metals: A New Role for Organic Polymers." Dr. A. J. Epstein also attended this meeting.
21. August 31, 1987, Dr. Dong-Pile Kang and Dr. Mun-Soo Yun of Korea Electrotechnology Research Institute visited Dr. MacDiarmid's laboratory.
22. September 6 to 11, 1987, Dr. G. C. Farrington attended the Sixth International Conference on Solid State Ionics in Garnisch, West Germany.
23. September 14 to 18, 1987, Dr. A. G. MacDiarmid gave an invited lecture at the International Society for Electrochemistry in Maastricht, The Netherlands. Title of talk given there: "Conducting Polymers".
24. September 17-18, 1987, Dr. D. Glatzhofer of E. I. du Pont de Nemours Company Wilmington visited the laboratory of Dr. A. J. Epstein at O.S.U.
25. September 20, 1987, Dr. A. G. MacDiarmid's laboratory was one of three labs featured at an Open House of the Chemistry Department concomitant with the opening of the Council for Chemical Research Meeting held in Philadelphia.
26. September 21&22, 1987, Dr. A. G. MacDiarmid and Dr. G. C. Farrington attended the Council for Chemical Research Conference in Philadelphia. Together they gave the talk "Revolutionary Conductors: Polymers and Ceramics."
27. September 21, 1987, Dr. Richard Kaner of UCLA visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry.
28. September 23, 1987, Dr. A. G. MacDiarmid gave a lecture entitled "Conducting Polymers" for the Natural Science Association at the University of Pennsylvania, Department of Chemistry.

29. September 24 to October 1, 1987, Dr. Nicolas Theophilou of BASF, West Germany, visited the laboratories of Dr. A. G. MacDiarmid and Dr. Farrington at the University of Pennsylvania and Dr. A. J. Epstein at OSU. Title of the talk given: "Highly Conducting Polyacetylene."

30. September 27-28, Dr. N. Theophilou of BASF, West Germany visited the laboratory of Dr. A. J. Epstein at O.S.U.

31. September 30, 1987, Dr. Lynden Clausen, Campus Representative for the Office of Naval Research visited the laboratory of Dr. A. G. MacDiarmid at the University of Pennsylvania, Department of Chemistry.

V. Publications

1. Published Papers

Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Insulator-to-Metal Transition in Polyaniline," Solid State Commun. **63**, 97 (1987), J.M. Ginder, A.F. Richter, A.G. MacDiarmid and A.J. Epstein.

"Transport Studies of Protonated Emeraldine Polymer: A granular Polymeric Metal System," Physical Review B **36**, 3475 (1987), F. Zuo, M. Angelopoulos, A.G. MacDiarmid, and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Microwave Response of Confined Soliton Pairs (Bipolarons) in (N-Methylphenazinium)_x (Phenazine)_{1-x} (Tetracyanoquinodimethanide)." Phy. Rev. Lett. **59**, 1760 (1987). H.H.S. Javadi, J.S. Miller and A.J. Epstein. [Supported in part by URI and in part by Du Pont Co.].

"Are Semiconducting Polymers Polymeric Semiconductors?: Polyaniline as an Example of 'Conducting Polymers'", Conducting Polymers, ed. L. Alcácer, pp. 121-140 (Reidel Publications, Dordrecht, Holland, 1987). A.J. Epstein, J.M. Ginder, A.F. Richter and A.G. MacDiarmid. (Supported in part by URI and in part by ONR Contract #N00014-83-K-0209.)

(ii) Kuan (Lockheed)

"Processable Conducting Polymers for Aerospace Applications," Proceed. Indust. and Eng. Chem. Symp., ACS National meeting, Spring 1987. S.I. Yaniger, R.E. Cameron, B.R. Mattes, L.A. Landis. [Supported in part by URI and in part by Lockheed internal funding].

(iii) Wnek (MIT/RPI)

"Influence of Oxidation State, pH, and Counterion on the Conductivity of Polyaniline," J. Phys. Chem., **91** (22) 5813 (1987). W.W. Focke, G.E. Wnek and Y. Wei. [Supported in part by URI and in part by Council for Scientific and Industrial Research of South Africa].

2. Papers Accepted/Submitted for Publication(a) Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"A Covalent Bond to Bromine in HBr Treated Polyaniline From X-Ray Diffraction," Synth. Met., in press (1987), B.K. Annis, A.H. Narten, A.G. MacDiarmid and A.F. Richter. [Supported in part by URI and in part by DOE contract DE-AC05-84OR21400].

"Photoexcitation of Polarons and Molecular Excitons in Emeraldine Base," Phys. Rev. Lett. submitted (1987), M.G. Roe, J.M. Ginder, P.E. Wigen, A.J. Epstein, M. Angelopoulos, and A.G. MacDiarmid. [Supported in part by URI and in part by NSF Grant No. DMR-85-19059].

(ii) Wnek (MIT/RPI)

"Reactions of n-type (Reduced) Polyacetylene with Alkyl Halides," Macromolecules, **20**(12), 0000 (1987), D.H. Whitney and G.E. Wnek. [Supported in part by URI, and in part by an ARCO Career Development Award.]

"Electrochemistry of Polyaniline: Consideration of a Dimer Model," Symp. Proc. Electroactive Polymers, eds., D. Ulrich and P. Prasad, in press (1987), W.W. Focke and G.E. Wnek. [Supported in part by URI and in part by the Council for Scientific and Industrial Research of South Africa.]

VI. Patents

Patents resulting from URI support

(i) Penn (MacDiarmid) and Lockheed (Yaniger)

"Production of Base-Type Conducting Polymers," S. Yaniger, A.G. MacDiarmid and M. Angelopoulos, Serial No. #UP-144, filed February 11, 1987.

(ii) Montclair State College (Humphrey)

"Conducting Polymers Films, Methods of Manufacture and Applications Thereof," B.D. Humphrey, M.L. Kasner and J.L. Isidor, Attorney Docket No. 12827, filed June 3, 1987.

(iii) MIT/RPI (Wnek)

"Substituted Acetylenic Polymers and Conductive Materials Formed Therefrom," G.E. Wnek and D.H. Whitney, Serial No. #US 4,672,093, June 9, 1987. (This patent is assigned to MIT).

VII. Contractual Administration

1. Prime Contract - University of Pennsylvania

The funding for the second half of the year (i.e. 3/187 to 9/30/87) was received 6/4/87. However, funding for the second year of the contract (i.e. 10/1/87 to 9/30/88) had not been received as of 9/30/87.

2. Subcontracts

a. As of 9/30/87 all modifications to subcontracts extending the performance period to 9/30/87 had been fully extended by all parties.

b. On September 9, 1987, Ms. Sandra Houck of the University of Pennsylvania, Office of Administration signed a subcontract with Richard Scammell of the Office of Sponsored Programs of Rensselaer Polytechnic Institute on behalf of Gary Wnek recently transferred to Rensselaer from MIT.

c. In the first week of October, Ms. Sandra Houck will be issuing new modifications to all subcontractors extending the performance period to 1/30/88. There will be no extension of funds to these subcontracts until the University of Pennsylvania has received funds for FY 87/88.

VIII. Changes in Personnel

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

Dr. Susan P. Ermer completed her post-doctoral research at the University of Pennsylvania and began working for Lockheed Corporation, California as of September 1, 1987.

David Swanson (a transfer student from Case Western) was given permission by the Graduate Committee to join Dr. MacDiarmid's research group effective September 1, 1987. There are now three graduate research students supported by the URI: Alan Richter, Elliot Scherr and David Swanson.

Paul Fazen and Jean Chey mentioned in the last report, are in their first year of graduate studies at Penn and as such are supported by Penn until June when they are assigned an advisor. Boris Vuchic an undergraduate Chemical Engineering Major left Dr. MacDiarmid's group to study at Oxford University in England.

b. Department of Materials Science and Engineering (Farrington)

Dr. Ching-min Wu continues as post-doctoral fellow on this program. One of the two students supported on the program, Mr. Matthew Walter, has completed his M.S. thesis on the relationship between electrochemical preparative conditions and the morphology of polyaniline. He accepted a position as Research Engineer at Ametek.

Jonathan Foreman and Hong Yang have begun research supported in full by URI funds. Gary Jones continues to do research supported in part by URI funds.

2. The Ohio State University

Department of Physics (Epstein)

Professor Eitan Ehrenfreund of the Technion Institute of Haifa, Israel was a visiting professor in our laboratories from July 1 to September 30, 1987. We had two student workers this summer quarter: Emily Engle and Angela Perry.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Dr. Stuart Yaniger has terminated his employment with the Lockheed Aeronautical Systems Company. The principal investigator for the URI project is still Dr. Teh Kuan with Dr. Randy Cameron and Mr. Ben Mattes as support.

4. Massachusetts Institute of Technology/Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Duncan Whitney completed his Ph.D. and now works at Polaroid Corp., Cambridge, Massachusetts. Walter Focke completed his Ph.D. and returned to NMIR in Pretoria, South Africa. Dr. Yen Wei is now an Assistant Professor at Drexel University, Philadelphia, Pennsylvania and continues interactions with Dr. A. G. MacDiarmid at the University of Pennsylvania. Dr. Gary Wnek completed the program at MIT and moved to Rensselaer over the summer. A graduate student at Rensselaer, Lynette Prezyna, has begun research supported in full by the URI under Dr. Wnek's guidance.

5. University of Rhode Island

Department of Chemistry (Yang)

Richard Cushman, Robert Clark, and Brian Schmitz were paid as half time graduate research assistants during the summer. Their work was supported in full starting September 1, 1987.

6. Montclair State College

Department of Chemistry (Humphrey)

During the summer months of the final quarter of the URI subcontract Dr. Humphrey had the full time aid of two research assistants, Otto Pfefferkorn (BS from MSC currently working at Biocraft, Inc.) and Gordon Kitora (BS from Gettysburg currently attending graduate school at Lehigh). Both worked full time at MSC from 6/1/87 to 9/1/87. This fall several MSC undergraduate students will benefit from URI purchased equipment: Heidi Weiss, Joseph Rizzi, Michael Ciarello, and Per Granered will all be utilizing equipment and chemicals purchased with URI funding.

IX. Fiscal Status
Expenditures and Commitments

A. University of Pennsylvania*: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	Budgeted 9/15/86-9/30/87	Total Spent & Committee 9/15/86-9/30/87	Available Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	499,426	227,618*
U of P (MSE) (Dr. G.C. Farrington)	231,565	168,604	62,961

*"Available Balance" for MacDiarmid and Farrington consists entirely of unexpended equipment monies. These funds must be used for salaries and supplies until we have received funds for the second year.

B. Subcontracts: The following represents monies paid on receipt of demand (i.e. bills) from participating subcontractors.

	Budgeted 9/15/86-9/30/87	Total* billed to date	Available Balance
OSU (Dr. A.J. Epstein)	867,116	564,249	302,867
Lockheed (Dr. T. Kuan)	87,037	87,037	-0-
MM Inc. (Ms. Marie Dolton)	37,143	34,577	2,566
Academic Sub- Contractors			
a. Dr. Wnek			
1. MIT	36,996	35,996	1,000
2. RPI	36,006	-0-	36,006
b. Univ Rhode Island (Dr. S. Yang)	31,862	7,849	24,013
c. Montclair State (Dr. B. Humphrey)	29,231	12,641	16,590

*Bills lag approximately 2-3 months behind actual expenditures, therefore this is an inflated figure. However, all subcontractors have attempted to hold back in spending in order to have funds available for use until second year funds are received by Penn.